AD 278 830

WADD-TR-60-782
PART IX

VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURES

PART IX — CORRELATION OF DISSOCIATION ENERGIES OF GASEOUS MOLECULES AND OF HEATS OF VAPORIZATION OF SOLIDS; HOMONUCLEAR DIATOMIC MOLECULES

TECHNICAL DOCUMENTARY REPORT No. WADD-TR-60-782, PART IX

MAY 1962

DIRECTORATE OF MATERIALS AND PROCESSES
(MATERIALS CENTRAL)
AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Project No. 7350, Task No. 735001

(Prepared under Contract No. AF 61(052)-225
by the Universite Libre de Bruxelles, Brussels, Belgium;
G. Verhaegen, F. E. Stafford, P. Goldfinger, M. Ackerman, Authors)

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Qualified requesters may obtain copies of this report from the Armed Services Technical Information Agency, (ASTIA), Arlington Hall Station, Arlington 12, Virginia.

This report has been released to the Office of Technical Services, U.S. Department of Commerce, Washington 25, D.C., in stock quantities for sale to the general public.

Copies of this report should not be returned to the Aeronautical Systems Division unless return is required by security considerations, contractual obligations, or notice on a specific document.

900 - July 1962 - 41-1788 & 1789

FOREWORD

This report was prepared by the University of Brussels, Brussels, Belgium under USAF Contract No. AF61(052)-225. The contract was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials," Task No. 735001, "Non-Graphitic." The work was administered under the direction of the Directorate of Materials and Processes, Deputy Commander/ Technology, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. Mr. F. W. Vahldiek was the project engineer.

This report covers work done from April 1961 to April 1962.

wADD Technical Report 60-782, Parts I, II, III, V, VI have already been published. Parts IV, VII, and VIII are in preparation.

ABSTRACT

Homonuclear diatomic molecules are classified according to the ratio $\alpha = \Delta H_o^\circ(\text{vap.M})/D\delta(M_2)$. For transition elements $\Delta H_o^\circ(\text{vap.M}) A - B\Sigma_i \epsilon_i$ (M). $\Sigma_i \epsilon_i$ (M) is the excitation energy of the free atom to a set of electronic levels; A and B are empirical parameters. Experimental conditions for observing unknown homonuclear diatomic molecules of transition elements are estimated for $\alpha = 2$ and 5, using a calculated self-consistent set of free energy functions.

PUBLICATION REVIEW

This technical documentary report has been reviewed and is approved.

FOR THE COMMANDER

W. G. RAMKE
Chief, Ceramics and Graphite Branch
Metals and Ceramics Laboratory
Directorate of Materials and Processes

TABLE OF CONTENTS

FIGURE EXPLANATIONS

Fig.1- $\alpha = \Delta H_o^o(\text{vap.M})/D_o^o(M_2)$ vs Z where $\Delta H_o^o(\text{vap.M})$ is the heat of vaporization of the monoatomic species, $D_o^o(M_2)$ the dissociation energy of the symmetric diatomic molecule and Z the atomic number. Triangles (Δ) indicate elements for which $0.5 \leq \alpha \leq 1.0$, crosses (X) those for which $1.2 \leq \alpha \leq 2.5$ and circles (O) those for which $\alpha \geq 5$.

Fig.2- Measured (0) and calculated (X) heats of vaporization in kcal/mole for the elements ranging from Ca to Zn. $\Delta H_o^o(\text{vap.M})_{calc} = 178 - 0.5 \sum_i \varepsilon_i(M)$ where $\sum_i \varepsilon_i(M)$ is the sum of the excitation energies to the lowest d^a, $d^{a-1}s^1$, $d^{a-2}s^2$, $d^{a-2}s^1p^1$ levels of the atom.

Fig.3- Measured (0) and calculated (X) values of $\Delta H_o^o(\text{vap.M})$ for Ni, Pd, Pt and elements of groups IB and IIB. Values are calculated according to the equation:

$$\Delta H_o^o(\text{vap.M}) = 131 - 1/4 \sum_i \varepsilon_i(M)$$

The ground state and the excited states yielding a total of two d, one s and one p bonding orbitals are the following :

Ni: $3d^8 4s^2(^3F)$(two d); $3d^8 4s(^2D)4p(^3F)$(one s, one p)

Cu: $3d^{10}4s(^2S)$(one s); $3d^{10}4p(^2P)$(one p); twice $3d^9 4s^2(^2D)$(one d)

Zn: $3d^{10}4s^2(^1S)$; $3d^{10}4s4d(^1D)$(one s, one d); $3d^9 4s^2 4p(^1P)$(one d, one p)

Pd: $4d^{10}(^1S)$; $4d^9 5s(^3D)$(one s,one d); $4d^9 5p(^3P)$(one d, one p)

Ag: $4d^{10}5s(^2S)$(one s);$4d^{10}5p(^2P)$(one p);twice $4d^9 4s^2(^2D)$(one d)
Cd: $4d^{10}5s^2(^1S)$;$4d^{10}5s5d(^1D)$(one s, one d);$4d^9 5s^2 5p(^1P)$(one d,one p)
Pt: $5d^9 6s(^3D)$(one d,one s);$5d^9 6p(X)$(one d, one p)
Au: $5d^{10}6s(^2S)$(one s);$5d^{10}6p$(one p);twice $5d^9 6s^2(^2D)$(one d)
Hg: $5d^{10}6s^2(^1S)$;$5d^{10}6s6d(^1D)$(one s,one d);$5d^9 6s^2 6p(^1P)$(one d,one p)

Fig.4- Energy level diagrams for V and Mn. The levels indicated correspond to the heat of vaporization, ΔH_o^o(vap.M), to atoms in their ground state: $d^{a-2}s^2$; to atoms in excited states: $d^{a-i}s^1$, $d^{a-2}s^1p^1$ and d^a; and to atoms in a promoted configuration; ΔH_o^o(vap.M) + 1/2 $\sum_i \varepsilon_i$(M); where $\sum_i \varepsilon_i$(M) is the sum of the excitation energies to the levels indicated. a is the number of peripheric electrons of the elements considered (a = 5 for V and a = 7 for Mn).

SUMMARY

In this paper two correlations are proposed. The first correlation classifies the forty odd known homonuclear diatomic molecules according to the ratio $\alpha = \Delta H_o^o(\text{vap.M})/D_o^o(M_2)$ (heat of vaporization of an atom/dissociation energy of the diatomic molecule). Values of α = 0.5 to 1, 1.2 to 2.5 and > 5 correspond to three categories each consisting of several whole groups of elements. The significance of this classification is discussed qualitatively.

The second correlation shows that $\Delta H_o^o(\text{vap.M})$ can be closely represented by $A - B\sum_i \epsilon_i(M).\sum_i \epsilon_i(M)$ is the energy necessary to excite the atoms to a promoted "configuration" composed of equal contributions of a well defined set of low lying electronic states of the free atom. A and B are empirical parameters. One set of electronic states is taken for Ca to Ni, Sr to Pd, and Ba to Pt with B = 1/2 and A = 178, 206., 230 kcal/ atom respectively ; another set of electronic levels and A = 131 kcal and B = 1/4 represent $\Delta H_o^o(\text{vap.M})$ for Ni, Cu, Zn Pd, Ag, Cd, Pt, Au, Hg.

Using the first classification, the experimental conditions are estimated for observation of the yet unknown homonuclear diatomic molecules of the transition elements. For this purpose a self consistent set of free energy functions has been calculated.

Manuscript released by authors April 1962 for publication as an WADD Technical Documentary Report.

1. Introduction.

Of the ninety odd possible homonuclear diatomic molecules, classical chemistry had identified about a dozen and had succeeded in measuring only a few of their dissociation energies, $D_o^o(M_2)$. In the twenties and thirties, many other molecules of this type were discovered by optical spectroscopy and in many cases accurate values of dissociation energies were measured. In the last decade, further homonuclear diatomic molecules have been discovered, principally by mass spectrometry, and the dissociation energies of these as well as of some previously known molecules have been obtained. Lattice energies, $\Delta H_o^o(\text{vap.M})$, on the other hand, are relatively well known for practically all elements : in many cases to 5% and better.

The purpose of this paper is to establish a correlation between $\Delta H_o^o(\text{vap.M})$ and $D_o^o(M_2)$ and a correlation between $\Delta H_o^o(\text{vap.M})$ and the position, Z, of an element in the periodic table.

These correlations are based on the presently available dissociation energies and heats of vaporization[1-26] listed in table 1. Up to Rn(Z = 86) quite satisfactory $D_o^o(M_2)$ are available for about 40 molecules ; seven rare gases do not form physically stable molecules ; the gaseous homonuclear diatomic molecules of 24 transition metals and 14 rare earths are as yet uncharacterized and give rise to a large gap in our knowledge.

While a few years ago the existence or observation of metal-metal molecules would have been surprising, today many such molecules have been observed and there is no reason to believe that like metal atoms cannot combine to form a molecule with a stable ground state. In fact, in cases already observed, interatomic forces are quite large and give rise to appreciable dissociation energies. As shown in table 2, the dissociation energies of the group IB molecules are comparable to those of the halogens.

It should be noted that even though D_0^o may be large, the vapor phase concentration of molecules can be quite small. Kronig[27] had proposed to distinguish between physical stability, i.e. D_0^o, of a given species and some measure of the concentration characteristic of its chemical stability. It is useful to introduce a quantitative measure of this latter magnitude and to define the term chemical stability as the free energy change for the most favorable net reaction of formation of the molecule. In the case of many metal-metal molecules, the physical stability is great, but experimental conditions practically never give rise to high concentrations of the molecules ; their chemical stability is always low.

It is therefore of great practical importance to know the experimental conditions under which yet unknown symmetric diatomic molecules might be observed. For this purpose a set of free energy functions have been estimated systematically, and the temperatures at which observable ratios p(molecule)/p(atom) may be expected have been calculated using the correlation found between ΔH_o^o(vap.M) and $D_o^o(M_2)$.

2. Correlation between dissociation energy and lattice energy.

a) The correlation.

For the elements Li, Na, K, Rb and Cs, whose molecules were known already in the thirties, Pauling[28] observed that

$$\alpha = \Delta H_o^o(\text{vap.M})/D_o^o(M_2) \approx 1.5 \qquad (1)$$

was almost constant.

When existing data for Cu_2, Ag_2 and Au_2 were verified[16] it was noted that α for this group was $1.8 \pm .1$. This prompted calculation of α for the remaining diatomic molecules. When α is plotted as a function of Z (Fig.1), three distinct almost horizontal bands are observed. Members of those bands which we call "categories" have similar electronic structures:

the first category $0.5 \leq \alpha \leq 1.0$, includes elements of groups VB(s^2p^3), VIB(s^2p^4) and VIIB(s^2p^5) ;

the second category, with $1.2 \leq \alpha \leq 2$, includes elements of groups IA(s^1), IB($d^{10}s^1$), IIIB(s^2p^1) and IVB(s^2p^2) ;

the third category, with $\alpha \geq 5$, includes elements of groups IIA(s^2) and IIB($d^{10}s^2$).

For category 1, D_o^o varies from 225(N_2) to 36 kcal/mole (I_2) while α varies from 0.5(N) to 1(Bi). For category 2, D_o^o varies from 142(C_2) to 10.8 kcal/mole (Cs_2) while α varies from 1.2(C) to 2.6(In). In both categories α is seen to increase systematically as one descends in the Periodic Table, but this increase is very small relative to the decrease of $D_o^o(M_2)$.

Some finer trends may be observed in Fig. 1 : there seems to be a slight systematic decrease in α from s^2p^3 to s^2p^4 and s^2p^5, also from s^2p^1 to s^1 and s^2p^2. The irregularities in group IIIB(Al) and IVB(Ge) may well be due to experimental inaccuracies.

The case of Cu, Ag and Au deserves closer attention. Starting with Cu, ΔH_o^o <u>decreases</u> from 80.8 kcal/mole to 68.3 for Ag, then increases to 87.3 for Au. The values of D_o^o are respectively 45.5, 37.6 and 51.5 kcal/mole with an uncertainty in the relative values of less than $\pm$ 2 kcal/mole. The resulting α, with an experimental uncertainty of only about $\pm$ 5% are 1.79, 1.82 and 1.70 and are seen to be sensibly constant. Further-

more it should be noted that α for K, Rb and Cs also is 1.8 ± 0.05 even though D_o^o is 4 to 5 times smaller than for IB group molecules.

b) Significance.

The value $\alpha = 0.50$ for light molecules of category 1 means of course that intermolecular bonding in the crystal lattice is completely negligible compared to the bond in the molecule. As one descends in the periodic table α increases towards 1, showing that the bonding to neighbouring atoms in the crystal lattice becomes as important as the bond in the molecule. It could be admitted that this is due as well to the influence of d-electrons as to that of the polarizability of these large atoms. This could be decided probably only by more quantitative estimates which are beyond the scope of this paper.

On the other hand, for the category 3 elements, with the quasi rare gas electronic configuration $s^2(^1S_0)$, one assumes that bonding in the gas phase is due to Van der Waals interactions or slight mixing with excited states causing a shallow potential minimum in what otherwise would be a repulsive curve. In the metal however, the bonding occurs presumably between atoms in a promoted configuration[29]. Thus the two phases have rather different types of bonds hence the

high values of α (> 5) observed in category 3. These values seem to show much larger and more irregular variations than those of categories 1 and 2. Whether this is a property of this category, or is due to the experimental inaccuracy of the correspondingly low D_0^o values is difficult to judge.

It is for category 2 that the correlation becomes really significant. The α values for group IA have been explained by Pauling[28] by assuming that the bonds in gas and metal are quite similar. In the gas, the s electrons of each atom combine to form the usual σ type covalent bond. In the metal this same bond is assumed to exist, but has a small amount of p character, and the increase of bond energy per atom pair in the metal is due to the "resonance" of the bond among the 14 nearest and next nearest neighbors.

On the basis of extensive data for the magnetic and physical properties of the metals, Pauling[30] has hypothesized that bonding in the metal is due to hybridization of all of the ns, np and (n-1)d orbitals. According to this theory, the metal bond in group IB would have 28% ($d^7s^1p^3$) and 72% ($d^8s^1p^2$) character and a valence of 5.56. The decrease, then increase in atomization energy in going from Cu to Ag to Au would be due to differences in accessibility of excited states.

In accordance with this idea, the lowest lying excited levels in Ag are much higher than in Cu or Au. This hypothesis plus the argument used in the case of Group IA implies that the bonds in the gaseous molecules have a great deal of p and d character. Presumably, this hybridization explains why the group IB gaseous molecules are so much more stable than those of group IA. In the case of B and Al the configuration to be assumed for the condensed phase bond is sp^2, (valence 3) while for Ga and In it is $d^9s^1p^3$ combined with $d^{10}s^1p^2$(valence 3.56). Hence here again the gaseous molecules are inferred to have bonds with mixed s and p character and the valence of the gaseous molecules would be inferred to be greater than unity and probably closer to the value 3.56 and 5.56 for groups IIIB and IB. These surprisingly high valencies would satisfy nicely the correlations between vibrational force constant and bond order advanced by Guggenheimer[31] and by Gordy[32].

3. Correlation between heats of vaporization of the transition elements and the promotional energy of the atoms.

Bonds of high valency by hybridization of orbitals have been assumed by Pauling[30] to explain various properties

of solid metals. Sheline[33] has made qualitative correlations between excitation energies of low-lying electronic states of the transition element atoms and the force constants of their diatomic gaseous hydrides. However, this correlation with an "excited"configuration" does not seem to have been used for a quantitative representation of lattice energies.

The variation of heats of vaporization in the third, fourth and fifth periods of the periodic table appear at first sight to be highly irregular (e.g. Figs 2 and 3). Similar trends in the stability of the corresponding solid carbides, silicides, nitrides, oxides and sulfides have been pointed out by Krikorian[34] and a similarity of the bonds in these compounds and the metals has been assumed.

A plot of the excitation energies (ε) of low lying electronic states of the elements of these periods, vs.Z shows however breaks which actually match some of the breaks in the plot ΔH_0^o(vap.M) vs. Z. If the assumption is made that the excitation energy to a configuration of high valency can be obtained as some average of the excitation energy to low-lying excited electronic states, a situation is found as shown in Fig.4 for the example of V and Mn. Whereas the heat

of vaporization from V to Mn drops from 122 to 67 kcal/g. atom, the sum: heat of vaporization plus half of the sum of excitation energies to the three states (d^a, $d^{a-1}s^1$, $d^{a-2}s^1p^1$), is constant within 4 kcals/g. atom. In the designation of excited states a represents the difference between the atomic number (Z) of the element and the atomic number of the preceding rare gas.

The lattice energies of the elements from Ca to Zn, from Sr to Cd, and from Ba to Hg may thus be represented by

$$\Delta H_o^o(\text{vap.M}) = A - B \sum_i \varepsilon_i(M) \qquad (1)$$

where the parameter A is the energy necessary to bring one atom from the crystal lattice into a promoted configuration and the parameter B characterizes the contribution of the different electronic states of the free atom to the energy of this promoted configuration.

Use of this equation is tantamount to the assumption that the bond energy of the promoted configuration in the lattice is constant for the elements of a given period.

For the period Ca to Ni, B = 0.5 has been chosen by trial and error. Then the best fit is obtained for A = 178 kcals/g atom. Measured and calculated values of $\Delta H_o^o(\text{vap.M})$ are displayed in Fig.2. The maximum disagreement, of the order of 15 kcals/mole occurs for Ca, Cr and Ni. This might be explained by the electronic configuration of these elements: Ca having no d electrons

in its ground state is not a transition element, $Cr(^7S_3)$, in contrast to the other elements of the third period has a $d^{a-1}s^4$ structure in its ground state, and Ni has a d^a level which corresponds to a complete d subshell, and is therefore a non-bonding state.

This correlation, as seen above, cannot be properly applied to Ni, Pd and Pt. It is therefore even less applicable to elements of groups IB and IIB. Owing to the significant differences in the electronic configurations of the three groups of elements, no coherent set of common electronic states can be found, and a different application of eq.1 was therefore expected.

For these elements the term $\sum_i \varepsilon_i(M)$ was chosen to represent the energy necessary to excite the atoms to a set of states which yield, with the ground state, a total of two d, one s, and one p bonding orbitals. The excited states used for the different elements are given in the legend to fig.3, which displays measured and calculated values of $\Delta H^o_o(vap.M)$ for Ni, Cu, Zn, Pd, Ag, Cd, Pt, Au and Hg.

The best agreement is achieved with A = 131 kcals/mole and B = 1/4, which is in keeping with random spin concepts. Even though the enthalpies vary from over 100 to 15 kcals/mole,

measured and calculated values, except for Pt, agree within 10 kcals/mole. This correlation also accounts for the surprising decrease and then increase in ΔH^{o}_{o}(vap.M) in going from Cu to Ag to Au.

For the transition elements of the other two long periods, the correlation is less definite than for the third period, the electronic levels, $d^{a-2}s^2$, $d^{a-2}sp$, $d^{a-1}s$ and d^{a} being less well known. Keeping B = 1/2 constant values of A = 206 and A = 250 kcals/mole give the best agreement for periods 4 and 5 respectively. Certain features of the known empirical data are well correlated as for instance the shift of the maximum of ΔH^{o}_{o}(vap.M) from group VA in the third and fourth periods (V, Nb) to group VIA(W) in the fifth period.

An extension of the present considerations to compounds seems promising and is being undertaken now[35]. Similar regularities seem to exist[23] also for heats of vaporization of the rare earth elements and oxides, with breaks in the plots of ΔH^{o}_{o}(vap.M) *vs.* Z at or near the point of the one half filled *f* shell ; the complex spectra of the rare earth elements however do not permit one to propose a simple correlation.

It is believed that this is the first quantitative correlation which, with a good approximation, represents the trends of lattice energies in an important part of the periodic

table.Perhaps the empirical choice of the states made in these correlations could be justified and further refined by a theoretical study of the problem. That excited states of volatile elements are systematically higher than those of refractory elements is a definite fact. An effort to develop a correlation based on thorough theoretical considerations seems therefore worthwhile.

4. Chemical stability of homonuclear diatomic molecules.

The value of α can be shown to correlate with temperature variation of the concentration of the molecules relative to the atoms in the saturated vapor. Consider

$$M_2(g) \rightleftharpoons 2\ M(s) \qquad -\Delta H_o^o(vap.M_2) \qquad (2)$$

$$M\ (s) \rightleftharpoons M\ (g) \qquad \Delta H_o^o(vap.M) \qquad (3)$$

$$M_2(g) \rightleftharpoons 2\ M(g) \qquad D_o^o(M_2) \qquad (4)$$

$$M\ (g) \rightleftharpoons M\ (s) \qquad -\Delta H_o^o(vap.M) \qquad (5)$$

Combining (2) and (3) or (4) and (5) we have

$$M_2(g) \rightleftharpoons M(g) + M(s) \qquad (6)$$

for which the enthalpy change is

$$\Delta H_o^o(vap.M) - \Delta H_o^o(vap.M_2) = D_o^o(M_2) - \Delta H_o^o(vap.M)$$

which can also be written as:

$$\Delta H_o^o(vap.M)\ (1 - \alpha)/\alpha \text{ with } \alpha = \Delta H_o^o(vap.M)/D_o^o(M_2)$$

From which:

$$\frac{R\ d\ \ln\ p(M)/p(M_2)}{d(1/T)} = -\ \Delta H_o^o(vap.M)(1 - \alpha)/\alpha \qquad (7)$$

From equation (7), if α is less than unity, the relative concentration of M_2 decreases with temperature. This is the case for the molecules well known at low temperatures. By our definition these are the molecules of category 1. If α is greater than unity, as in the case of C_2 and the metal-metal molecules for example, the relative concentration of molecules in the <u>saturated</u> vapor increases with increasing temperature. Such molecules may be called the "high temperature molecules".

That monomer-dimer ratios in saturated vapors may increase or decrease with temperature has been discussed in detail and also explained for the case of halides by Brewer[36]. It has also been shown by Drowart and Goldfinger[37] that the dimer-tetramer ratio for group VB elements may increase or decrease with temperature depending on whether vaporization is from the pure element or from a compound.

Apparently, the transition elements form molecules of the "high temperature" group. The most recent techniques have not been applied to the study of the transition elements, except for preliminary experiments on four elements: Mn, Ni, Cr and Pd. It is interesting to see to what extent these techniques might yield useful information. This discussion will assume techniques which can detect one molecule in 10^5 atoms: for example mass spectrometry or spectroscopy.

Assuming these experimental limits, we now calculate what temperatures and metal vapor pressures will be necessary to observe molecules if α be equal to 2 (category 2) or 5 (category 3).

The free energy change corresponding to the overall reaction (6) is given by

$$\Delta F_{(6)} = RT \ln p(M_2)/p(M) = \Delta H_o^o(\text{vap.M}) - \Delta H_o^o(\text{vap.}M_2) + T\Delta(\text{fef})$$
$$= \Delta H_o^o(\text{vap.M})(1 - \alpha)/\alpha + T\Delta(\text{fef}) \qquad (8)$$

where(fef), the free energy function, is equal to $(F_T^o - H_o^o)/T$. $\Delta F_{(6)}$ can be considered as a quantitative expression of the chemical stability for homonuclear diatomic molecules.

5. Calculation of the change in the free energy function for the reaction $M_2(g) \rightleftharpoons M(g) + M(s)$.

(a) The free energy functions of the diatomic molecules are calculated according to the equation

$$\text{fef}_{M_2} = R\left[7/2 \ln T + 5/2 \ln M + 2 \ln d\right] - 14{,}308 + \text{fef}_{vib} + \text{fef}_{el} \qquad (9)$$

where T is the temperature in °K ; M is the atomic mass of the element constituting the molecule expressed in a.m.u. ; d the internuclear distance in $\mathring{A}$ and R = 1,987 cal.degree^{-1}mole^{-1}, the gas constant. Vibrational free energy functions, fef_{vib}, for the harmonic oscillator are given in tables by Pitzer[38],

Numerous correlations have been proposed, between internuclear distances and force constants, and between force constants, dissociation energies and internuclear distances. These correlations have been reviewed by Clementi[39] who also proposed a relation between interatomic distances and atomic numbers. However, for the transition elements, none of the necessary parameters are known and the following procedure has been adopted: twice the atomic radii for single covalent bonds given by Pauling[30] have been used for the interatomic distances ; the values of ω were chosen by analogy with those known for the molecules of the elements at the beginning and at the end of each period. Disregarding at first the electronic free energy function, fef_{el}, concerning which practically nothing is known, one obtains values for fef_{M_2} varying by not more than $\pm$ 1 e.u. about the average values given in table 3 ; the agreement is as good for cases for which good calculations have been made as for groups IA and VIB, of course taking into account fef_{el} in the the latter case.

(b) For the solids, $fef_{[M]}$, and for monoatomic vapors, fef_M, the data, were taken from the table of Stull and Sinke[1]. For the third period the sum $fef_M + fef_{[M]}$ at 1000°K is given in table 4 as an example. Apparently the average given in table 4 is good within $\pm$ 1.5 e.u. At higher temperatures and for periods 4 and 5 the fluctuations are somewhat larger. For the rare earths there occurs a maximum lying 6 e.u. above the average.

(c) For Δfef of eq.(8) it is proposed to calculate an average value for each period and for each temperature as given in table 3, where $\langle \Delta fef \rangle = \langle fef_{[M]} \rangle + \langle fef_M \rangle - \langle fef_{M_2} \rangle + 2.2$. In this way instead of a risk of addition or errors one expects rather a partial cancellation. In fact, the sum $fef_{[M]} + fef_M$ may be higher than the average for two reasons: (1) many low lying atomic energy states, (2) low lattice vibration frequencies. In the first case, many low lying energy states may also be expected in the molecule, in the second, e.g. by Baughan's rule,[40] a low value of ω and a large value of d and fef_{M_2} is expected and vice versa. Of course it is unrealistic to take an electronic degeneracy of 1 for the molecule ; we have taken 3 as an average and have added therefore 2.2 to Δ fef.

It seems thus that for Δ fef an uncertainty of about $\pm$ 2 e.u. could result from fef_{el} (electronic degeneracy between 1 and 10) and a total uncertainty of $\pm$ 4 to 5 e. u. is a fair estimate. It is not believed however that a better guess can be made without definite data at least on vibration frequencies and electronic states of molecules. An improvement could be made if an approximate value of D_{M_2} is known. To a large value of D_{M_2}, or small α will correspond a large ω and a small d and hence a smaller fef_{M_2} ; one could thus calculate a first

approximation of $D_0^o(M_2)$ using $\langle \Delta \text{ fef} \rangle$, then correct accordingly Δ fef and recalculate a second approximation of $D_0^o(M_2)$. As the estimate stands it could lead to an error in $D_0^o(M_2)$ of 4 - 5, 8 - 10 or 12 - 15 Kcal at 1000, 2000 or 3000°K respectively or to an uncertainty of $\pm$ 1 $\log_{10}$ unit in the estimates of table 5.

6. Conclusions.

In this paper two correlations have been proposed. The first relates the dissociation energy of homonuclear diatomic molecules to the lattice energy of the corresponding elements. The second relates the lattice energy to the promotional energy of a configuration composed of low-lying excited levels of the atoms.

If Pauling's theory of a resonating bond for the alkali metals can be extended to all elements of categories 2 and 3, and the correlation between lattice energies and promotional energies finds a sound theoretical basis (maybe based on energies of interaction of electrons with random spins) it would also be possible to understand more fully the bonding between isolated atoms and predict dissociation energies of yet unknown molecules.

Unfortunately, existing data are still insufficient to permit one to predict values of α (and hence dissociation energies of the homonuclear diatomic molecules) for the transition elements, as the two correlations overlap only for group IB whose elements have complete d subshells. For this group however, one finds that the dissociation energies of the diatomic molecules are related with the availability of bonding low-lying excited levels of the atoms.

It actually therefore seems important to obtain experimental data on the transition element diatomic molecules to have an idea of the incidence of d electrons on bond energies. To this effect from eq.(8) and the free energy functions given in table 3, we have calculated temperatures and pressures of monoatomic species at which P_M/p_{M_2} reaches 10^5 for $\alpha = 2$ and $\alpha = 5$. These values are given in table 5.

As can be seen from this table, the experimental conditions required are very severe for most cases if $\alpha = 5$, and for many cases even if $\alpha = 2$. Indeed, conventional mass spectrometric techniques will have to be seriously improved to permit one either to reach the temperatures or to handle the pressures in the extreme cases.

REFERENCES.

1. Stull and Sinke, "Thermodynamic Properties of the Elements" Advances in Chem.Ser. (1956). 18.

2. Lewis, Randall, Pitzer and Brewer, "Thermodynamics" McGraw Hill, New York (1961).

3. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand, New York (1950).

4. Gaydon, "Dissociation Energies", 2d ed. (revised), Chapman and Hall Ltd, London (1953).

5. Drowart and Inghram "Mass Spectrometry Applied to High Temperature Chemistry" High Temperature Technology", McGraw Hill, New York (1960).

6. (a) "Selected Values of Chemical Thermodynamic Properties", circ.500 of the National Bureau of Standards (1952).
(b) Giauque and Johnston, J.Am.Chem.Soc.(1929) 51, 2300.
(c) Kanda, Bull.Chem.Soc.Jap. (1937) 12, 511.
(d) Giauque and Powell, J.Am.Chem.Soc.(1939) 61, 1970.

7. Drowart and Honig, J.Phys.Chem.(1957) 61, 980.

8. Verhaegen and Drowart (to be published).

9.. Chupka, Argonne National Laboratory Rep.(1957) 5786, 73.

10. Drowart, Burns, DeMaria and Inghram, J.Chem.Phys. (1959) 31, 1131.

11. Soulen, Sthapitanonda and Margrave, J.Phys.Chem. (1955) 59, 132.

12. Colin, Goldfinger and Jeunehomme, Nature (1960) 187, 408.

13. Thorn and Winslow, J.Phys.Chem. (1961) 65, 1297.

14. Brewer, U.C.R.L. (1955) 2854.

15. Kubaschewski and Heymer, Acta Meta.(1960) 8, 416.

16. Ackerman, Stafford and Drowart, J.Chem.Phys.(1960) 33, 1784.

17. To be published.

18. Hampson and Walker, XVIIIth International Congress of Pure and Applied Chemistry, Montreal (1961) ; J.Res.Natl. Bur.Stand. (1961) 65.A, 289

19. Hampson and Walker, Communication at the XVIIIth International Congress of Pure and Applied Chemistry, Montreal (1961).
Dreger and Margrave, J.Phys.Chem.(1960) 64, 1323.

20. Porter, J.Chem.Phys. (1961) 34, 583.
Colin, Ind.Chim.Belg. (1961) 26, 51.

21. Daane and Spedding, Abst.A.C.S. Meeting, Chicago,(Sept. 1958).

22. Jeunehomme, Thesis, Université Libre de Bruxelles (1961).

23. White, Walsh, Goldstein and Dever, J.Phys.Chem.(1961)65, 1404.

24. Savage, Hudson and Spedding, J.Chem.Phys.(1959) 30, 221.

25. Spedding, Havak and Daane, Trans. A.I.M.E.(1958) 212, 379.

26. Ackermann and Rauh, J.Chem.Phys. (1962) 36, 448.

27. Kronig, "The Optical Basis of the Theory of Valency", Cambridge (1935).

28. Pauling, Physic.Rev. (1938) 54, 899.

29. The expression promoted "configuration" seems to be the most suitable.

30. Pauling,"The Nature of the Chemical Bond", Cornell, Ithaca (1960).

31. Guggenheimer Proc.Phys.Soc., London (1946) 58, 456.

32. Gordy, J.Chem.Phys. (1946) 14, 305.

33. Sheline, J.Chem.Phys. (1950) 18, 927.

34. Krikorian, University of California U.C.R.L. (1955) 2888.

35. Colin and Goldfinger, Part $\underline{X}$, to be published.

36. Brewer, Natl.Nucl.En.Series,(1946) Div.4, Vol.19B,p.261, McGraw Hill.

37. Drowart and Goldfinger, J.Chim.Phys.(1958) 53, 721.

38. Pitzer, Quantum Chemistry, Prentice Hall Inc. Englewood Cliffs, New York (1953).

39. Clementi, Ann.Chim.(Rome)(1960) 50, 548.

40. Baughan, Trans.Faraday Soc. (1952) 48, 121.

41. Moore, "Atomic Energy Levels". Circ.467 National Bureau of Standards (1949).

TABLE I

Li 38.1 25.8 1.48	Be 76.9 14 (7) 5.16											B 128 (8,9) 65 (8,9) 1.97	C 169.6 142.1 (10) 1.19	N 113.3 225.0 0.504	O 60.0* 118.0 0.509	F 19.3 36.8 0.524
Na 25.9 17.5 1.48	Mg 35.3 7 (11) 5.04											Al 76.9 46 1.67	Si 107 74 1.45	P 79.5 116 0.685	S 65.9 (12) 100.9 (12) 0.65	Cl 31.7 57.1 0.555
K 21.6 (13) 11.9 (13) 1.82	Ca 42.1 5 (14) 8.4	Sc 79.7 (26)	Ti 112.1	V 122.0	Cr 93.5 (15)	Mn 66.9	Fe 98.9	Co 101.2	Ni 102.3	Cu 80.8 45.5 (16) 1.78	Zn 31.1 6 5.2	Ga 64.7 32 2.02	Ge 89.3 65 1.37	As 68.7 89.3 0.769	Se 55.4 (17) 77 (17) 0.72	Br 26.9 45.4 0.592
Rb 19.8 11.3 1.75	Sr 39.3*	Y 97.6 (26)	Zr 145.7	Nb 176.9	Mo 157.1	Tc 155*	Ru 144*	Rh 144* (18)	Pd 89.9 (19)	Ag 68.3 37.6 (16) 1.82	Cd 26.9 2.1 12.8	In 57.1 22.4 2.55	Sn 72.0 45.8 1.57	Sb 61.7 70.6 0.87	Te 46 (20) 52.8 (20) 0.87	I 25.6 35.6 0.720
Cs 19.1 10.4 1.83	Ba 42.8*	La 104.1 (26)	Hf 168	Ta 186.7	W 199.7	Re 185.55	Os 160*	Ir 159.6* (18)	Pt 134.7 (18)	Au 87.3 51.5 (16) 1.69	Hg 15.4 1.4 11.0	Tl 43.2 14 (7) 3	Pb 47.0 (22) 23 2.05	Bi 49.6 46 1.1	Po 34.6* 35.4* 0.98	At 22* 22* 1.0
		Ce 96.4 (21) (298)	Pr 77.3 (23) (298)	Nd 76.6 (23)	Pm	Sm 49.6 (24) (298)	Eu 42.1 (25) (298)	Gd 83.9 (23) (298)	Tb 87.0 (23) (298)	Dy 61.6 (23) (298)	Ho 69.5 (23) (298)	Er 66.4 (23) (298)	Tm 57.6 (24) (298)	Yb 40.0 (24) (298)	Lu 94.7 (23) (298)	

Legend to Table 1.

Under the chemical symbols are listed in order: the enthalpies of vaporization, the dissociation energies of the homonuclear diatomic molecules when available, and the value of $\alpha = \Delta H_o^o(\text{vap.M})/D_o^o(M_2)$. Data not otherwise marked were taken from[1-5] and when necessary reduced to 0°K with data in[6]. Beneath some recent data, reference numbers are indicated in brackets. Estimated reduction to 0°K is marked[*]; where a reasonable reduction did not seem possible the temperature (°K) is given in brackets.

TABLE 2. Comparison of Dissociation Energies of Diatomic Molecules of Elements of Group IB and of the Halogens.

Molecule	D_o^o(kcal/mole)[16]	Molecule	D_o^o(kcal/mole)[4]
Cu_2	45.5	Cl_2	57.1
Ag_2	37.6	Br_2	45.4
Au_2	51.5	I_2	35.6

TABLE 3.

Mean values of free energy functions.

Period		1000°K	2000°K	3000°K
Sc - Zn	$-\langle fef_{M_2} \rangle$ *	61.0	66.9	70.7
	$-\langle fef_{M+[M]} \rangle$	52.9	61.8	68.0
	$\langle \Delta fef \rangle$	10	7	5
Y - Cd	$-\langle fef_{M_2} \rangle$ *	65.1	71.2	74.8
	$-\langle fef_{M+[M]} \rangle$	55.3	63.3	69.8
	$\langle \Delta fef \rangle$	12	10	7
La - Hg	$-\langle fef_{M_2} \rangle$ *	68.7	74.9	78.5
	$-\langle fef_{M+[M]} \rangle$	57.6	64.4	71.7
	$\langle \Delta fef \rangle$	13	13	9

* $\langle fef_{M_2} \rangle$ does not take into account the electronic quantum weight of the molecule and thus:

$$\langle \Delta fef \rangle = -\langle fef_{M_2} \rangle + \langle fef_{M + [M]} \rangle + 2.2$$

TABLE 4.

Element	$-\,fef_{[M]}^{(1)}$	$-\,fef_{M}^{(1)}$	Element	$-\,fef_{[M]}^{(1)}$	$-\,fef_{M}^{(1)}$
Ca	50.26		Co	53.81	
Sc	53.55		Ni	54.45	
Ti	53.55		Cu	50.69	
V	58.77		Zn	52.21	
Cr	50.58		Ga	56.95	
Mn	52.62		Ge	51.40	
Fe	53.50		As	53.09	

TABLE 5

Temperatures and pressures of monoatomic species for which

$$p_{M_2} / p_M = 10^{-5}$$

Element	$\alpha = 2$		$\alpha = 5$	
	T°K	$- \log p_M$	T°K	$- \log p_M$
Ca	600	9.5	1050	3.2
Sc	1250	7.3	2200	1.5
Ti	1850	5.8	3250	0.6
V	2050	5.3	3600	0.1
Cr	1500	6.1	2600	0.7
Mn	1000	7.5	1750	1.6
Fe	1600	6.0	2800	0.8
Co	1650	5.9	2850	0.7
Ni	1650	6.0	2900	0.6
Cu	1250	7.4	2200	1.7
Zn	450	3.7	750	3.1
Sr	600	8.5	350	4.4
Y	1500	8.0	2600	2.0
Zr	2250	7.0	4000	-
Nb	2950	5.1	4000	-
Mo	2500	6.2	4000	-
Tc	2450	6.1	4000	-

TABLE 5 (CONT'D)

	T°K	- log p_M	T°K	- log p_M
Rn	2250	5.9	4000	-
Rb	2000	6.8	3950	0.1
Pd	1300	8.6	2200	2.7
Ag	1000	8.3	1600	2.9
Cd	300	13.4	600	3.8
Ba	600	10.1	950	4.5
La	1350	9.4	2250	3.3
Hf	2450	7.6	4000	-
Ta	2900	6.7	4000	-
W	3100	5.4	4000	-
Re	2900	6.6	4000	-
Os	2350	6.8	4000	-
Ir	2350	7.0	4000	-
Pt	1900	7.8	3600	0.9
Au	1200	9.2	1950	3.3
Hg	-	-	350	3.3

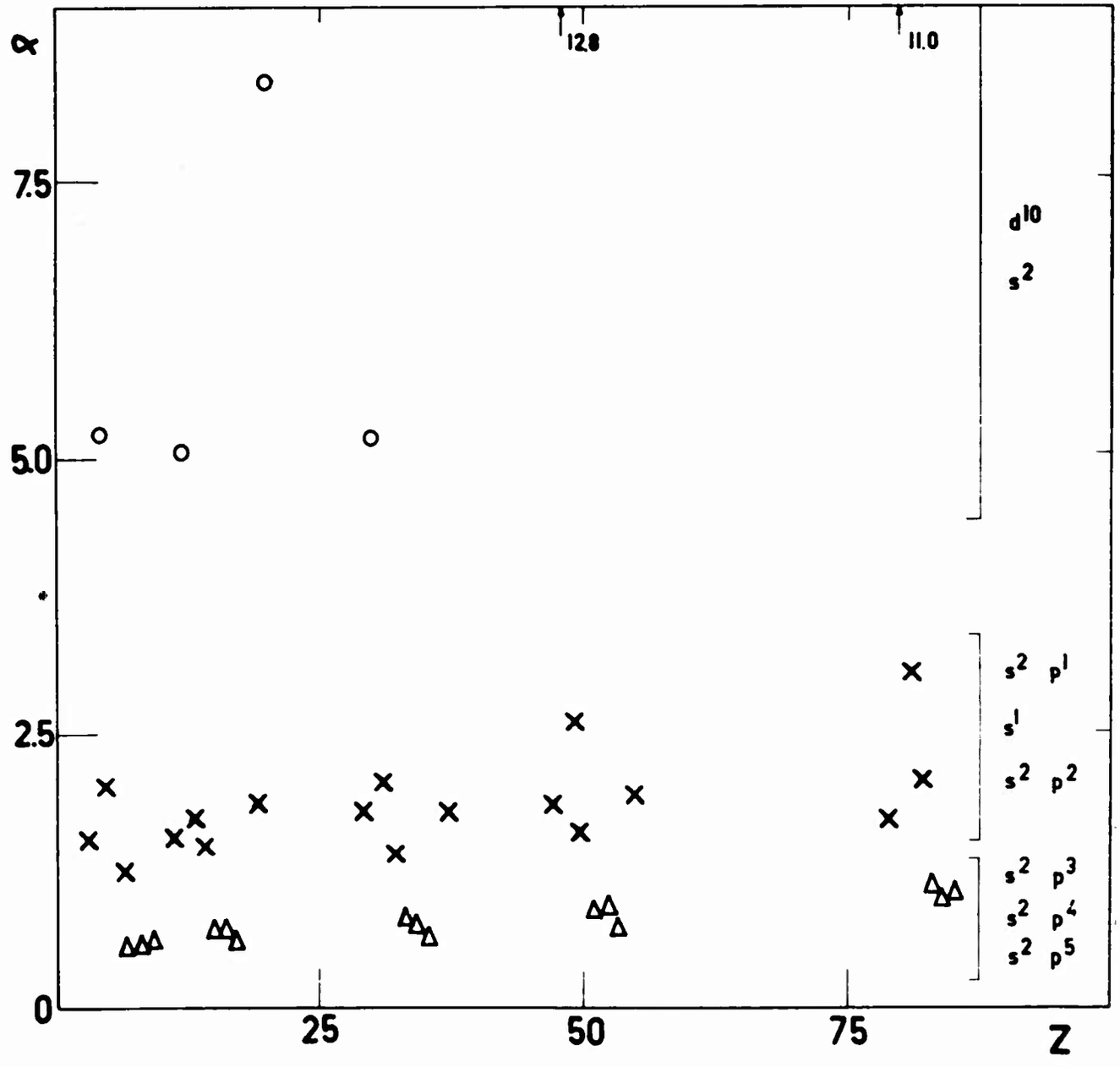

Figure 1

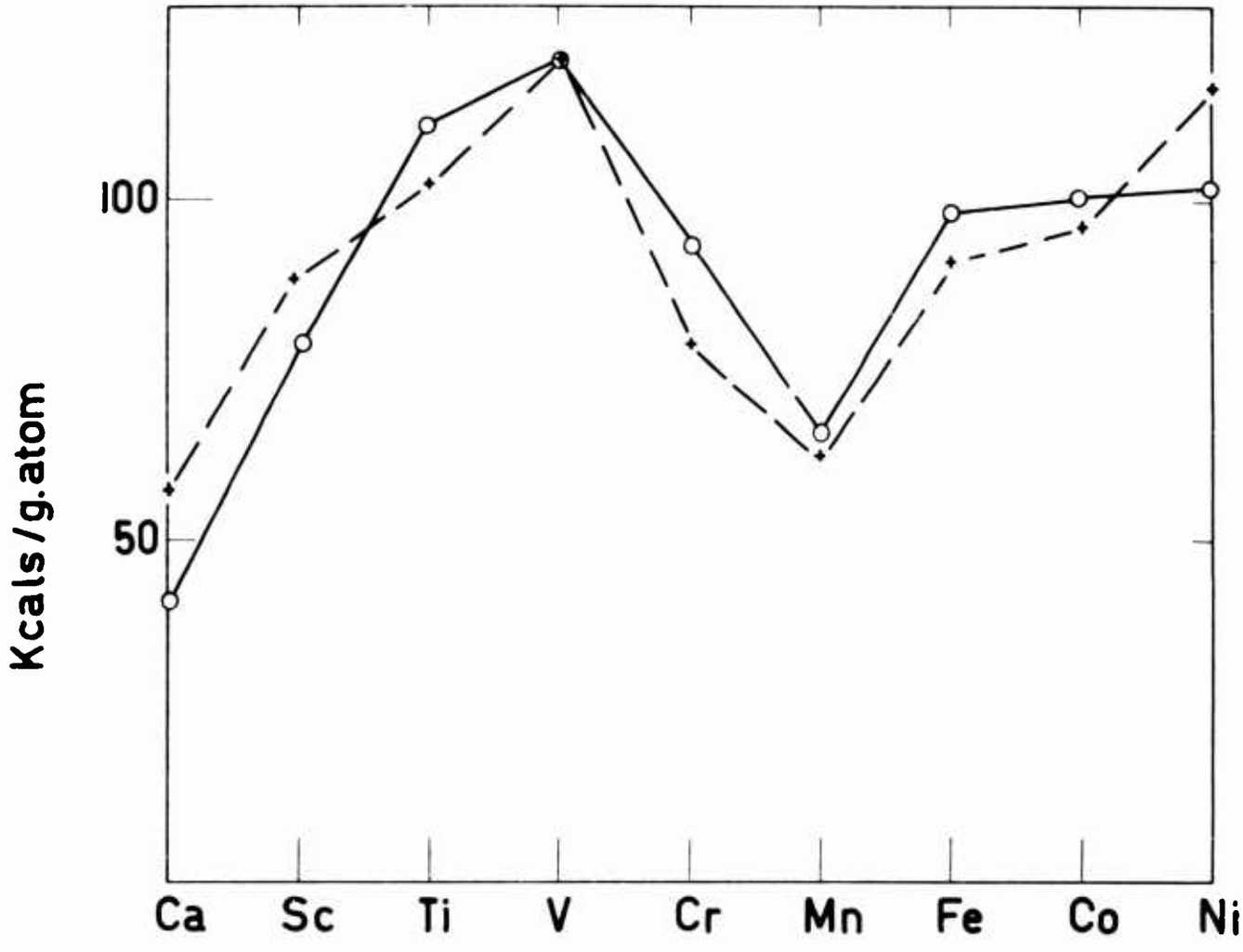

Figure 2

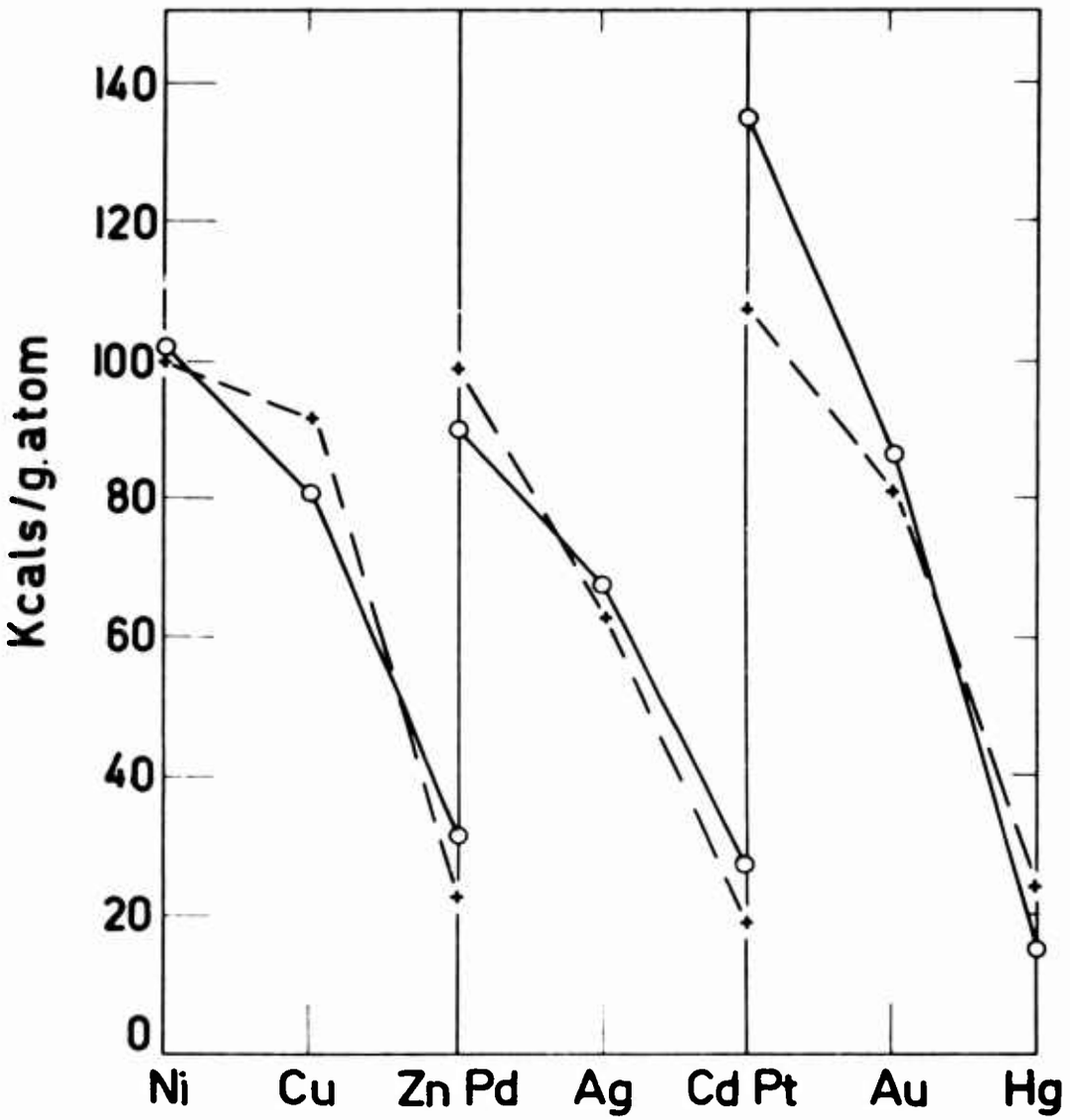

Figure 3

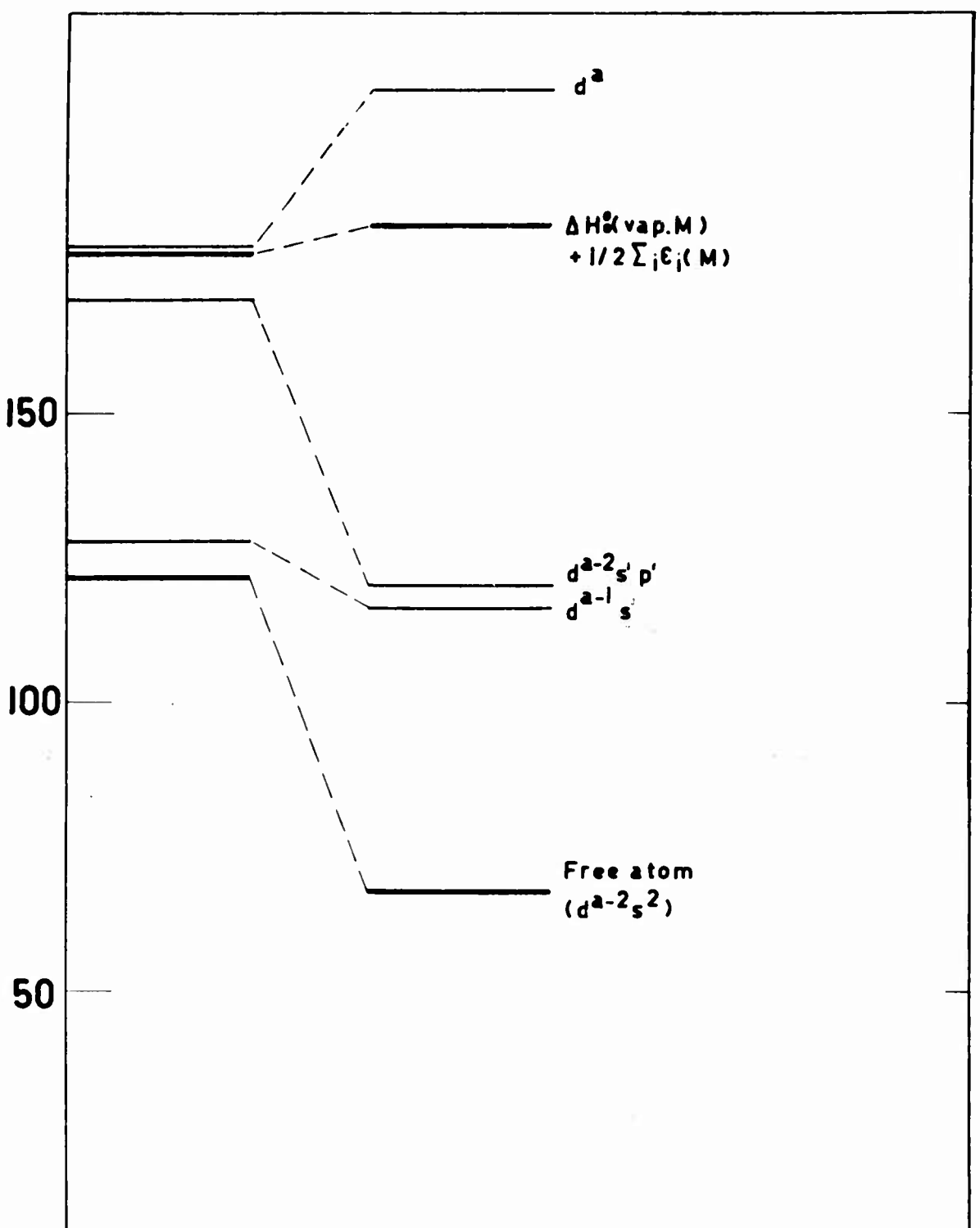
d^a
ΔH°_{sa}(vap.M)
$+ 1/2 \sum_i \varepsilon_i$(M)
150
$d^{a-2}s' p'$
$d^{a-1}s'$
100
Free atom
($d^{a-2}s^2$)
50
Lattice
V
Mn

Figure 4

Aeronautical Systems Division, Dir/Materials and Processes, Metals and Ceramics Lab, Wright-Patterson AFB, Ohio.
Rpt Nr WADD-TR-60-782, Pt IX. VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURES: Correlation of Dissociation Energies of Gaseous Molecules and of Heats of Vaporization of Solid Homonuclear Diatomic Molecules. Interim Report, May 62, 40p incl illus., tables, 41 refs.

Unclassified Report

Homonuclear diatomic molecules are classified according to the ratio $\alpha = \Delta H^{\circ}_{o}(vap.M)/D^{\circ}_{o}(M_2)$. For transition elements $\Delta H^{\circ}_{o}(vap.M) A-3\Sigma_i \epsilon_i$

(over)

(M). $\Sigma_i \epsilon_i (M)$ is the excitation energy of the free atom to a set of electronic levels; A and B are empirical parameters. Experimental conditions for observing unknown homonuclear diatomic molecules of transition elements are estimated for $\alpha = 2$ and 5, using calculated self-consistent set of free energy functions.

1. Vaporization
2. High temperature research
3. Compounds and alloys

I. AFSC Project 7350, Task 735001
II. Contract AF 61 (052)-225
III. Universite Libre de Bruxelles, Brussels, Belgium
IV. G. Verhaegen, et al.
V. Aval fr OTS
VI. In ASTIA collection

Aeronautical Systems Division, Dir/Materials and Processes, Metals and Ceramics Lab, Wright-Patterson AFB, Ohio.
Rpt Nr WADD-TR-60-782, Pt IX. VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURES: Correlation of Dissociation Energies of Gaseous Molecules and of Heats of Vaporization of Solids Homonuclear Diatomic Molecules. Interim Report, May 62, 40p incl illus., tables, 41 refs.

Unclassified Report

Homonuclear diatomic molecules are classified according to the ratio $\alpha = \Delta H^{\circ}_{o}(vap.M)/D^{\circ}_{o}(M_2)$. For transition elements $\Delta H^{\circ}_{o}(vap.M) A-3\Sigma_i \epsilon_i$

(over)

(M). $\Sigma_i \epsilon_i (M)$ is the excitation energy of the free atom to a set of electronic levels; A and B are empirical parameters. Experimental conditions for observing unknown homonuclear diatomic molecules of transition elements are estimated for $\alpha = 2$ and 5, using calculated self-consistent set of free energy functions.

1. Vaporization
2. High temperature research
3. Compounds and alloys

I. AFSC Project 7350, Task 735001
II. Contract AF 61 (052)-225
III. Universite Libre de Bruxelles, Brussels, Belgium
IV. G. Verhaegen, et al.
V. Aval fr OTS
VI. In ASTIA collection

Aeronautical Systems Division, Dir/Materials and Processes, Metals and Ceramics Lab, Wright-Patterson AFB, Ohio.
Rpt Nr WADD-TR-60-782, Pt IX. VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURES: Correlation of Dissociation Energies of Gaseous Molecules and of Heats of Vaporization of Solids Homonuclear Diatomic Molecules. Interim Report, May 62, 40p incl illus., tables, 41 refs.

Unclassified Report

Homonuclear diatomic molecules are classified according to the ratio $\alpha = \Delta H_o^o(\text{vap.M})/D_o^o(M_2)$. For transition elements $\Delta H_o^o(\text{vap.M}) A-B\Sigma_i \tilde{\epsilon}_i$ (M). $\Sigma_i \epsilon_i$ (M) is the excitation energy of the free atom to a set of electronic levels; A and B are empirical parameters. Experimental conditions for observing unknown homonuclear diatomic molecules of transition elements are estimated for $\alpha = 2$ and 5, using calculated self-consistent set of free energy functions.

(over)

1. Vaporization
2. High temperature research
3. Compounds and alloys

I. AFSC Project 7350, Task 735001
II. Contract AF 61 (052)-225
III. Universite Libre de Bruxelles, Brussels, Belgium
IV. G. Verhaegen, et al.
V. Aval fr OTS
VI. In ASTIA collection

Aeronautical Systems Division, Dir/Materials and Processes, Metals and Ceramics Lab, Wright-Patterson AFB, Ohio.
Rpt Nr WADD-TR-60-782, Pt IX. VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURES: Correlation of Dissociation Energies of Gaseous Molecules and of Heats of Vaporization of Solids Homonuclear Diatomic Molecules. Interim Report, May 62, 40p incl illus., tables, 41 refs.

Unclassified Report

Homonuclear diatomic molecules are classified according to the ratio $\alpha = \Delta H_o^o(\text{vap.M})/D_o^o(M_2)$. For transition elements $\Delta H_o^o(\text{vap.M}) A-B\Sigma_i \tilde{\epsilon}_i$ (M). $\Sigma_i \epsilon_i$ (M) is the excitation energy of the free atom to a set of electronic levels; A and B are empirical parameters. Experimental conditions for observing unknown homonuclear diatomic molecules of transition elements are estimated for $\alpha = 2$ and 5, using calculated self-consistent set of free energy functions.

(over)

1. Vaporization
2. High temperature research
3. Compounds and alloys

I. AFSC Project 7350, Task 735001
II. Contract AF 61 (052)-225
III. Universite Libre de Bruxelles, Brussels, Belgium
IV. G. Verhaegen, et al.
V. Aval fr OTS
VI. In ASTIA collection

Aeronautical Systems Division, Dir/Materials and Processes, Metals and Ceramics Lab, Wright-Patterson AFB, Ohio.
Rpt Nr WADD-TR-60-782, Pt IX. VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURES: Correlation of Dissociation Energies of Gaseous Molecules and of Heats of Vaporization of Solids Homonuclear Diatomic Molecules. Interim Report, May 62, 40p incl illus., tables, 41 refs.

Unclassified Report

Homonuclear diatomic molecules are classified according to the ratio $\alpha = \Delta H^{\circ}_{o}(vap.M)/D^{\circ}_{o}(M_2)$. For transition elements $\Delta H^{\circ}_{o}(vap.M) A-B \Sigma_i \tilde{\epsilon}_i$

(over)

(M). $\Sigma_i \epsilon_i$ (M) is the excitation energy of the free atom to a set of electronic levels; A and B are empirical parameters. Experimental conditions for observing unknown homonuclear diatomic molecules of transition elements are estimated for $\alpha = 2$ and 5, using calculated self-consistent set of free energy functions.

1. Vaporization
2. High temperature research
3. Compounds and alloys
- I. AFSC Project 7350, Task 735001
- II. Contract AF 61 (052)-225
- III. Universite Libre de Bruxelles, Brussels, Belgium
- IV. G. Verhaegen, et al.
- V. Aval fr OTS
- VI. In ASTIA collection

Aeronautical Systems Division, Dir/Materials and Processes, Metals and Ceramics Lab, Wright-Patterson AFB, Ohio.
Rpt Nr WADD-TR-60-782, Pt IX. VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURES: Correlation of Dissociation Energies of Gaseous Molecules and of Heats of Vaporization of Solids Homonuclear Diatomic Molecules. Interim Report, May 62, 40p incl illus., tables, 41 refs.

Unclassified Report

Homonuclear diatomic molecules are classified according to the ratio $\alpha = \Delta H^{\circ}_{o}(vap.M)/D^{\circ}_{o}(M_2)$. For transition elements $\Delta H^{\circ}_{o}(vap.M) A-B \Sigma_i \tilde{\epsilon}_i$

(over)

(M). $\Sigma_i \epsilon_i$ (M) is the excitation energy of the free atom to a set of electronic levels; A and B are empirical parameters. Experimental conditions for observing unknown homonuclear diatomic molecules of transition elements are estimated for $\alpha = 2$ and 5, using calculated self-consistent set of free energy functions.

1. Vaporization
2. High temperature research
3. Compounds and alloys
- I. AFSC Project 7350, Task 735001
- II. Contract AF 61 (052)-225
- III. Universite Libre de Bruxelles, Brussels, Belgium
- IV. G. Verhaegen, et al.
- V. Aval fr OTS
- VI. In ASTIA collection

Aeronautical Systems Division, Dir/Materials and Processes, Metals and Ceramics Lab, Wright-Patterson AFB, Ohio.
Rpt Nr WADD-TR-60-782, Pt IX. VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURES: Correlation of Dissociation Energies of Gaseous Molecules and of Heats of Vaporization of Solids Homonuclear Diatomic Molecules. Interim Report, May 62, 40p incl illus., tables, 41 refs.

Unclassified Report

Homonuclear diatomic molecules are classified according to the ratio $\alpha = \Delta H^{o}_{o}(vap.M)/D^{o}_{o}(M_2)$. For transition elements $\Delta H^{o}_{o}(vap.M) A-B \Sigma_i \epsilon_i$ (M). $\Sigma_i \epsilon_i$ (M) is the excitation energy of the free atom to a set of electronic levels; A and B are empirical parameters. Experimental conditions for observing unknown homonuclear diatomic molecules of transition elements are estimated for $\alpha = 2$ and 5, using calculated self-consistent set of free energy functions.

(over)

1. Vaporization
2. High temperature research
3. Compounds and alloys

I. AFSC Project 7350, Task 735001
II. Contract AF 61 (052)-225
III. Universite Libre de Bruxelles, Brussels, Belgium
IV. G. Verhaegen, et al.
V. Aval fr OTS
VI. In ASTIA collection

Aeronautical Systems Division, Dir/Materials and Processes, Metals and Ceramics Lab, Wright-Patterson AFB, Ohio.
Rpt Nr WADD-TR-60-782, Pt IX. VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURES: Correlation of Dissociation Energies of Gaseous Molecules and of Heats of Vaporization of Solids Homonuclear Diatomic Molecules. Interim Report, May 62, 40p incl illus., tables, 41 refs.

Unclassified Report

Homonuclear diatomic molecules are classified according to the ratio $\alpha = \Delta H^{o}_{o}(vap.M)/D^{o}_{o}(M_2)$. For transition elements $\Delta H^{o}_{o}(vap.M) A-B \Sigma_i \epsilon_i$ (M). $\Sigma_i \epsilon_i$ (M) is the excitation energy of the free atom to a set of electronic levels; A and B are empirical parameters. Experimental conditions for observing unknown homonuclear diatomic molecules of transition elements are estimated for $\alpha = 2$ and 5, using calculated self-consistent set of free energy functions.

(over)

1. Vaporization
2. High temperature research
3. Compounds and alloys

I. AFSC Project 7350, Task 735001
II. Contract AF 61 (052)-225
III. Universite Libre de Bruxelles, Brussels, Belgium
IV. G. Verhaegen, et al.
V. Aval fr OTS
VI. In ASTIA collection